

Lecture on First-principles Computations (8): Local Density Approximation and Generalized Gradient Approximations.

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Adiabatic connection construction of $E_{xc}[n(\mathbf{r})]$

The exchange correlation energy functional:

$$E_{xc}[n] = \frac{1}{2} \int d^3 r n(\mathbf{r}) \int d^3 r' \frac{\bar{n}_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

The XC energy can be interpreted as the Coulomb interaction energy between the electron and its XC hole.

$$\epsilon[n](\mathbf{r}) = \frac{1}{2} \int d^3 r' \frac{\bar{n}_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

The energy density per electron $\epsilon[n](\mathbf{r})$ at a given point \mathbf{r} is fully specified via the average XC hole $\bar{n}_{xc}(\mathbf{r}, \mathbf{r}')$.

The exchange-correlation hole

$$\begin{aligned}\epsilon[n](\mathbf{r}) &= \frac{1}{2} \int d^3 r' \frac{\bar{n}_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} = \frac{1}{2} \int d^3 u \frac{\bar{n}_{xc}(\mathbf{r}, \mathbf{r} + \mathbf{u})}{|\mathbf{u}|} \\ &= \frac{1}{2} \int du \left(\frac{u^2}{u} \right) \int d\Omega_{\mathbf{u}} \bar{n}_{xc}(\mathbf{r}, \mathbf{r} + \mathbf{u}) \\ &= \frac{1}{2} \int du u \langle \bar{n}_{xc}(\mathbf{r}, \mathbf{r} + \mathbf{u}) \rangle_{\Omega_{\mathbf{u}}}\end{aligned}$$

Angular-integrated exchange-correlation hole

The detailed angular-dependence of the XC hole is irrelevant, only the angular-integrated value matters.

O. Gunnarsson & B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).

The spin scaling relation

For exchange energy:

$$E_x[n_\uparrow, n_\downarrow] = E_x[n_\uparrow, 0] + E_x[0, n_\downarrow]$$

For spin-degenerate system: $n_\uparrow = n_\downarrow = n/2$

$$E_x[n] = E_x[n/2, n/2] = E_x[n/2, 0] + E_x[0, n/2] = 2E_x[n/2, 0]$$

Therefore,

$$E_x[n_\uparrow, n_\downarrow] = \frac{1}{2} (E_x[2n_\uparrow] + E_x[2n_\downarrow])$$

Popular functionals

- Local Density Approximation (LDA)
 - Vosko, Wilk, Nusair (VWN), 1980;
 - Perdew & Zunger (PZ), 1981;
 - Perdew & Wang (PW), 1992;
- Generalized Gradient Approximation (GGA)
 - Lee, Yang, Parr (LYP), 1988;
 - Becke (B88, B97, BLYP), 1988, 1997;
 - Perdew, Burke, Ernzerhof (PBE), 1996
- Meta-GGA
 - Tao, Perdew, Staroverov, Scuseria (TPSS), 2003
 - Strongly Constrained and Appropriately Normed functional (SCAN) (Sun, Ruzsinszky, Perdew), 2015
- Hybrid density functionals
 - B3LYP, 1993; PBE0, 1996;
 - Heyd, Scuseria, Ernzerhof (HSE), 2003

Jacob's ladder in DFT (John Perdew, 2001)



Hell -- The Hartree world

And Jacob went out from Beersheba, and went toward Haran. And he lighted upon a certain place, and tarried there all night, because the sun was set; and he took of the stones of that place, and put them for his pillows, and lay down in that place to sleep. And he dreamed, and behold a ladder set up on the earth, and the top of it reached to heaven: and behold the angels of God ascending and descending on it.

Genesis, 28.10-12

J. P. Perdew and K. Schmidt, in
“*Jacob's ladder of Density Functional Approximations for the Exchange-Correlation Energy*”,
2001

Local spin density approximation (LSDA)

$$E_{xc}^{\text{LSDA}}[n_{\uparrow}, n_{\downarrow}] = \int d^3 r n(\mathbf{r}) \epsilon_{xc}^{\text{HES}}(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})),$$



$\epsilon_{xc}^{\text{HES}}(n_{\uparrow}, n_{\downarrow})$: Exchange-correlation energy per electron of homogeneous electron gas (HEG)

$$\epsilon_{xc}^{\text{HES}}(n_{\uparrow}, n_{\downarrow}) = \epsilon_x^{\text{HES}}(n_{\uparrow}, n_{\downarrow}) + \epsilon_c^{\text{HES}}(n_{\uparrow}, n_{\downarrow})$$

For spin degenerate systems: $n_{\uparrow} = n_{\downarrow} = n/2$

$$\epsilon_x(n) = \epsilon_x(n/2, n/2) = -(3/4 \pi) k_F, \quad k_F = (3\pi^2 n)^{1/3}$$

Exchange energy functional in LSDA

$$E_x[n_\uparrow, n_\downarrow] = \frac{1}{2} (E_x[2n_\uparrow] + E_x[2n_\downarrow]) \leftarrow \text{Spin scaling relation}$$

$$E_x^{\text{LDA}}[n] = \int d^3 r n(\mathbf{r}) \epsilon_x^{\text{HES}}(n(\mathbf{r})) = -\frac{3(3\pi)^{1/3}}{4\pi} \int d^3 r n(\mathbf{r})^{4/3}$$

Introduce the spin polarization: $\zeta(\mathbf{r}) = \frac{n_\uparrow(\mathbf{r}) - n_\downarrow(\mathbf{r})}{n_\uparrow(\mathbf{r}) + n_\downarrow(\mathbf{r})}$

$$n_\uparrow(\mathbf{r}) = n(\mathbf{r}) (1 + \zeta(\mathbf{r}))/2, n_\downarrow(\mathbf{r}) = n(\mathbf{r}) (1 - \zeta(\mathbf{r}))/2$$

$$E_x^{\text{LSDA}}[n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r})] = \frac{1}{2} (E_x[n(\mathbf{r})(1 + \zeta(\mathbf{r}))] + E_x[n(\mathbf{r})(1 - \zeta(\mathbf{r}))])$$

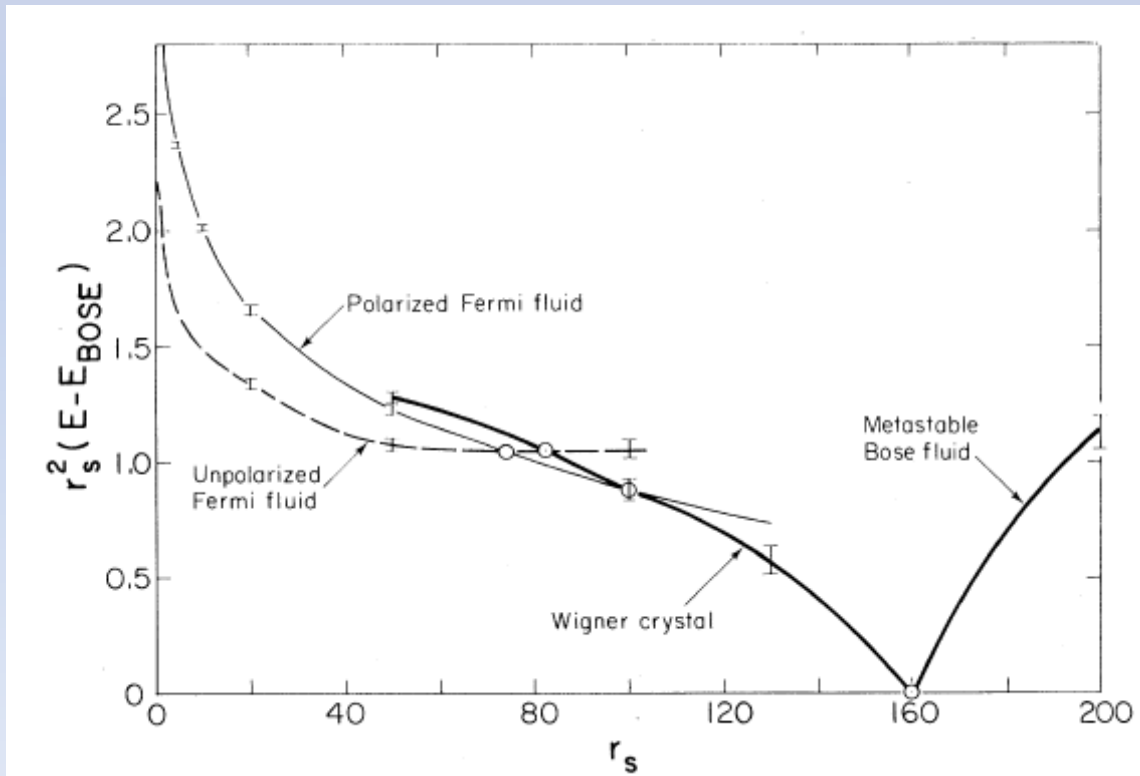
Exchange energy functional in LSDA

$$E_x^{\text{LDA}}[n_\uparrow, n_\downarrow] = \int d^3 r n(\mathbf{r}) \epsilon_x^{\text{LDA}}(n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r}))$$

$$\begin{aligned} \epsilon_x^{\text{LDA}}(n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r})) &= \epsilon_x^{\text{LDA}}(n(\mathbf{r})) \frac{[1 + \zeta(\mathbf{r})]^{4/3} + [1 - \zeta(\mathbf{r})]^{4/3}}{2} \\ &= - \frac{3(3\pi^2 n(\mathbf{r}))^{1/3}}{4\pi} \frac{[1 + \zeta(\mathbf{r})]^{4/3} + [1 - \zeta(\mathbf{r})]^{4/3}}{2} \end{aligned}$$

Exact numerical results

- An analytical evaluation of the **exact** ground-state energy of 3D HES is not possible.
- Numerically exact results are available via the diffusion quantum Monte Carlo (QMC) method.
- Knowing the exact ground-state energy of HES is a key to the success of density functional theory (DFT).



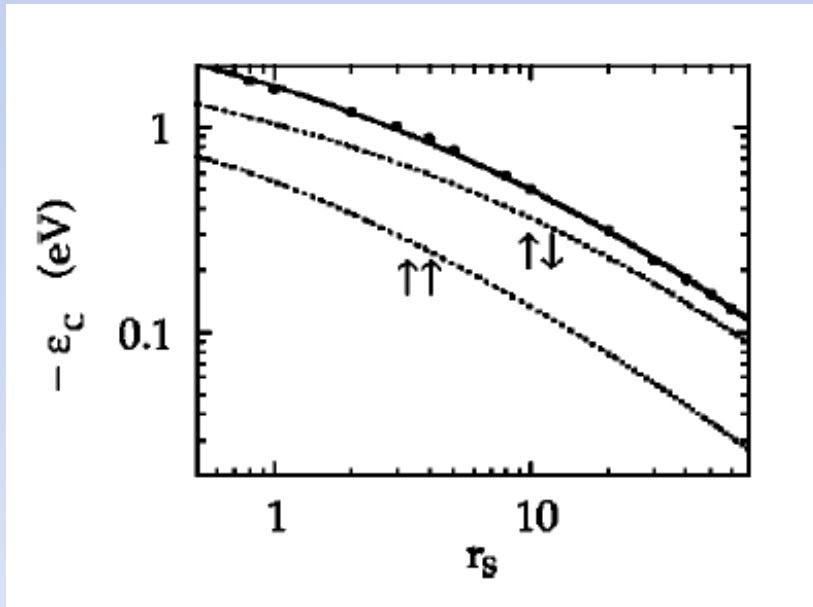
“Ground State of the Electron Gas by a Stochastic Method”

D. M. Ceperley and B. J. Adler,
Phys. Rev. Lett. **45**, 566 (1980).

Correlation energy functional in LSDA

$$E_c^{\text{LDA}}[n_\uparrow, n_\downarrow] = \int d^3 r n(\mathbf{r}) \epsilon_c^{\text{HES}}(n(\mathbf{r}), \zeta(\mathbf{r}))$$

Exact $\epsilon_c^{\text{HES}}(n, \zeta)$ is not known analytically, but there are plenty of approximate results from theory, and numerically exact results from QMC.



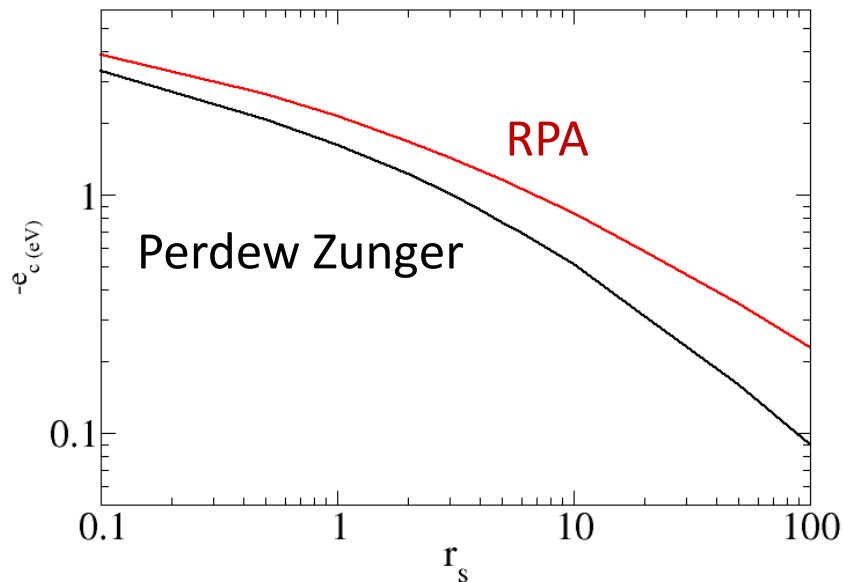
Ceperley & Adler, PRL, 1980

$$\epsilon_c[n_\uparrow, n_\downarrow] = \epsilon_{c,\uparrow\uparrow}[n, \zeta] + \epsilon_{c,\uparrow\downarrow}[n, \zeta]$$

Parameterization of the LDA correlation energy functional

Perdew-Zunger LDA (Phys. Rev. B **23**, 5048 (1981))

$$\epsilon_c = \begin{cases} -0.0480 + 0.031 \ln(r_s) - 0.0116 r_s + 0.0020 r_s \ln(r_s), & \text{for } r_s < 1 \\ -0.1423 / (1 + 1.9529 \sqrt{r_s} + 0.3334 r_s), & r_s > 1 \end{cases}$$



Other parameterization also exists.

- Vosko-Wilk-Nusiar (VWN), 1980
- Perdew-Wang, 1992

LDA and GGAs

- Local(spun)-density approximation (LDA)

$$E_{xc}^{\text{LDA}}[n_{\uparrow}, n_{\downarrow}] = \int d^3 r n(\mathbf{r}) \epsilon_{xc}^{\text{HES}}(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})),$$

- Generalized gradient approximations (GGA)

$$E_{xc}^{\text{GGA}}[n_{\uparrow}, n_{\downarrow}] = \int d^3 r f(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r}), |\nabla n_{\uparrow}(\mathbf{r})|, |\nabla n_{\downarrow}(\mathbf{r})|)$$

LDA is unique, but there are many different flavors of GGA

Generalized gradient approximation (GGA)

- $$E_{xc}^{GGA}[n_{\uparrow}, n_{\downarrow}] = \int d^3 r f(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r}), |\nabla n_{\uparrow}(\mathbf{r})|, |\nabla n_{\downarrow}(\mathbf{r})|)$$
$$= \int d^3 r n(\mathbf{r}) \epsilon_x^{\text{HES}}(n(\mathbf{r})) F_{xc}(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r}), |\nabla n_{\uparrow}(\mathbf{r})|, |\nabla n_{\downarrow}(\mathbf{r})|)$$

F_{xc} : enhancement factor

Limiting case :

$$f(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r}), 0, 0) = n(\mathbf{r}) \epsilon_x^{\text{HES}}(n(\mathbf{r}))$$

For the exchange energy, spin-scaling relation exists:

$$E_x[n_{\uparrow}, n_{\downarrow}] = \frac{1}{2} (E_x[2n_{\uparrow}] + E_x[2n_{\downarrow}])$$

Thus only spin-unpolarized cases need to be explicitly considered.

GGA versus GEA

$$F_{xc} = F_x + F_c$$

Define the m -th order dimensionless density gradient

$$s_m = \frac{|\nabla^m n|}{(2k_F)^m n}, \quad k_F = (3\pi^2 n)^{1/3}$$

Lowest order expansions of F_x in terms of s_m are known:

$$F_x = 1 + \frac{10}{81} s_1^2 + \frac{146}{2025} s_2^2 + \dots$$

This is called “gradient expansion approximation” (GEA) which does not work well (violation of sum rules)

Generalized gradient approximations:

$$F_x(s) = 1 + \alpha(s)s^2, \quad s = s_1$$

Perdew-Burke-Ernzerhof GGA

Generalized Gradient Approximation Made Simple

John P. Perdew, Kieron Burke,* Matthias Ernzerhof

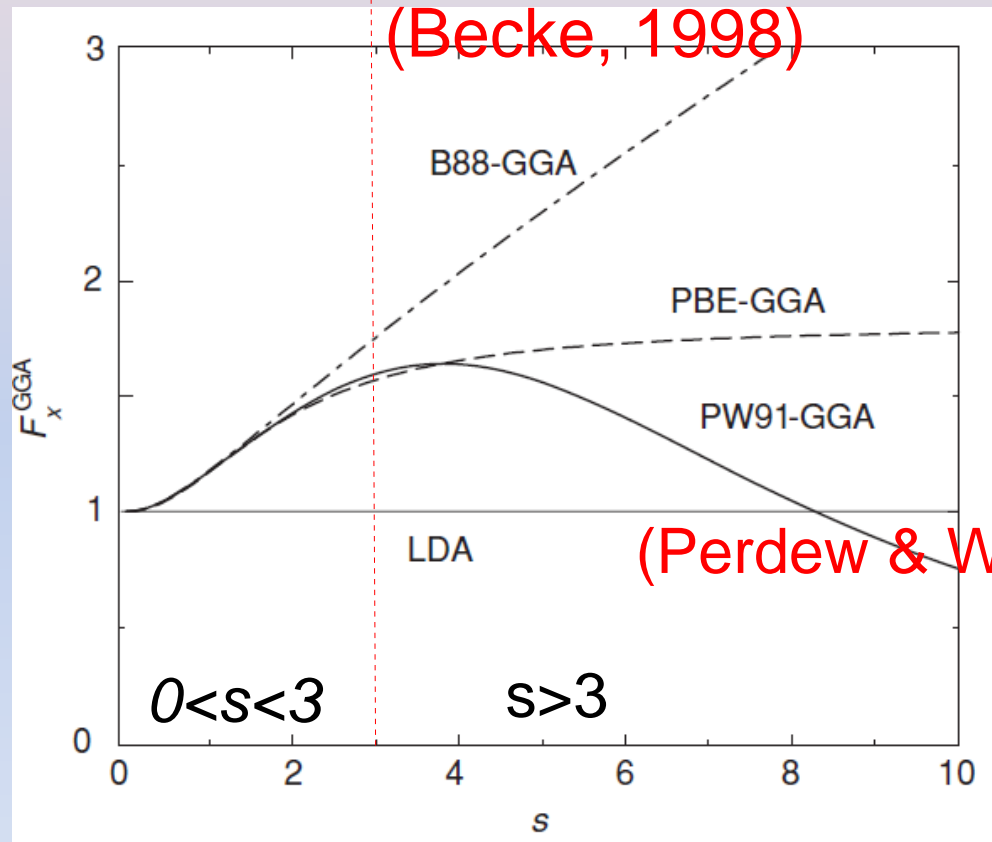
Department of Physics and Quantum Theory Group, Tulane University, New Orleans, Louisiana 70118
(Received 21 May 1996)

Generalized gradient approximations (GGA's) for the exchange-correlation energy improve upon the local spin density (LSD) description of atoms, molecules, and solids. We present a simple derivation of a simple GGA, in which all parameters (other than those in LSD) are fundamental constants. Only general features of the detailed construction underlying the Perdew-Wang 1991 (PW91) GGA are invoked. Improvements over PW91 include an accurate description of the linear response of the uniform electron gas, correct behavior under uniform scaling, and a smoother potential. [S0031-9007(96)01479-2]

Phys. Rev. Lett. 77, 3865 (1996)

The PBE GGA is constructed to satisfy known conditions of the exact functional as much as possible, and makes a compromise between the solids and molecules.

GGA exchange enhancement factor



$$F_x^{\text{PBE}}(s) = 1 + \kappa - \kappa / \left(1 + \frac{\mu s^2}{\kappa}\right) \quad \kappa = 0.804, \quad \mu = 0.2195$$

GGA correlation enhancement factor

Lower-order gradient expansion for the correlation energy is also known:

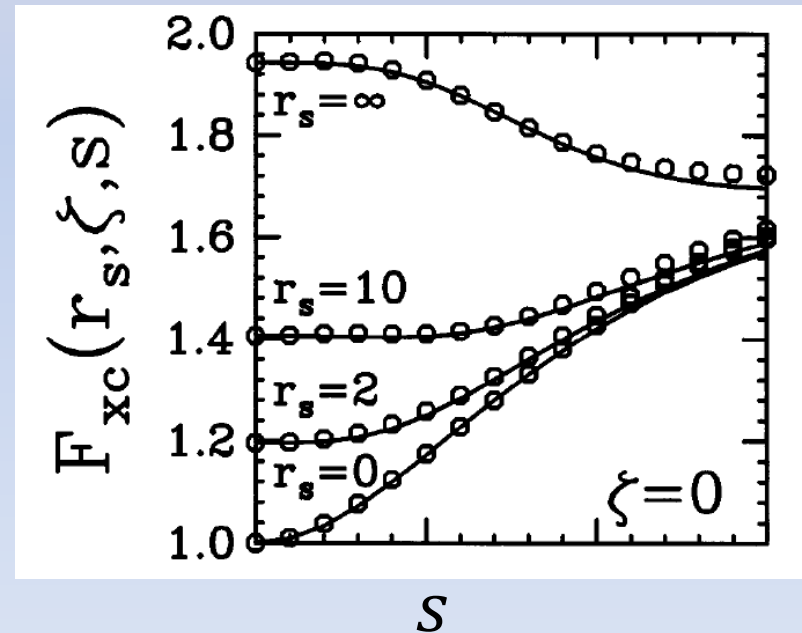
$$F_c = \frac{\epsilon_c^{\text{LDA}}(n)}{\epsilon_x^{\text{LDA}}(n)} (1 - 0.21951s_1^2 + \dots)$$

Similar to the exchange case, GGA F_c also adopts a more general form:

$$F_c = F_c(n, s, \zeta)$$

$$F_{xc} = F_x + F_c$$

The PBE F_{xc} enhancement factor



GGA versus LDA

- For solids, LDA generally overbinds, while GGA underbinds.
- For molecules, LDA overbinds too much. The accuracy of LDA is not sufficiently good for chemistry. GGA improves over LDA significantly for molecules.

$$E_b = E(\text{molecules}) - \sum_i E_i^{\text{atom}}$$

LDA underestimates the XC energy for systems with rapidly varying densities, especially for atoms. GGA corrects LDA, and improves the total energy of atoms more than that of molecules, and hence the binding energy increases.

Different GGAs are constructed to satisfy different conditions, and hence may perform better or worse for a given system. There is no single GGA that is universally better than others for all problems.

Exact exchange, LDA exchange, GGA exchange

- Exact exchange


$$E_x^{\text{exact}}[\{\phi_{l\sigma}\}] = - \sum_{l,m,\sigma}^{\text{occ}} \langle \phi_{l\sigma} \phi_{m\sigma} | \phi_{m\sigma} \phi_{l\sigma} \rangle$$

- LDA exchange

$$E_x^{\text{LDA}}[n] = \int n(\mathbf{r}) \epsilon_x^{\text{HES}}(n(\mathbf{r})) d^3r = - \frac{3(3\pi)^{1/3}}{4\pi} \int n^{4/3}(\mathbf{r}) d^3r$$

- GGA exchange

$$s(\mathbf{r}) = |\nabla n(\mathbf{r})| / 2k_F n$$

$$E_x^{\text{GGA}}[n, \nabla n] = \int n(\mathbf{r}) \epsilon_x^{\text{HES}}(n(\mathbf{r})) F_x(s(\mathbf{r})) d^3r$$


Exact exchange, LDA exchange, GGA exchange

$$E_x^{\text{GGA}}[n, \nabla n] = \int n(\mathbf{r}) \epsilon_x^{\text{HES}}(n(\mathbf{r})) F_x(s(\mathbf{r})) d^3r$$

E.g. $F_x^{\text{PBE}}(s) = 1 + \kappa - \kappa / (1 + \mu s^2 / \kappa)$

Error compensation

$$\left| \Delta \left(E_x^{\text{LDA/GGA}} + E_c^{\text{LDA/GGA}} \right) \right| < \left| \Delta \left(\Delta E_{x/c}^{\text{LDA/GGA}} \right) \right|$$

Self interaction (SI) not canceled in LDA/GGA

$$E^{\text{SI}}[\{\phi_{l\sigma}\}] = - \sum_{l\sigma}^{\text{occ}} \langle \phi_{l\sigma} \phi_{l\sigma} | \phi_{l\sigma} \phi_{l\sigma} \rangle$$